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the amount of ash in coal and (3) the rate of accumulation of vegetation leading to the formation of coal. To the casual observer it appears that there is not enough mineral matter in average coal to allow for the amount of atmospheric dust which would be deposited with the vegetation in the time ordinarily assumed to be required for the accumulation of vegetable matter in coal.

From everyday observation the universal presence of atmospheric dust is apparent. The work of Free,<sup>1</sup> Huntington,<sup>2</sup> Reid<sup>3</sup> and others emphasizes the quantity as being much greater than commonly supposed. However, it is not the amount of dust *in* the air, but the amount that is *caught* in standing water or by vegetation that is significant in the present connection.

An average of the analyses of ash content for representative coals of the United States given by M. R. Campbell<sup>4</sup> shows the following:

GRADE OF COAL	PERCENTAGE OF ASH
Lignite .....	8.25
Sub-bituminous .....	7.8
Bituminous .....	8.7
Semi-bituminous .....	8.7
Semi-anthracite .....	11.75
Anthracite .....	13.7

The last two averages are based only upon a few analyses.

It has been stated in text-books that about 9,000 years is required for the accumulation of sufficient vegetable matter to make one foot of bituminous coal. There is no reason to believe that this estimate is not at least approximately correct.

If dust was deposited from air during the coal-making periods at a rate of  $\frac{1}{4000}$  inch per year—which at the present does not seem excessive—9 inches of dust would be accumulated during the period of 9,000 years. Conse-

quently, with every foot of bituminous coal there should be 9 inches of atmospheric dust; that is, every foot of average coal would be about 75 per cent. dust. Even  $\frac{1}{40000}$  inch of dust a year would result in coal with  $7\frac{1}{2}$  per cent. dust. And this does not take into account the vegetable mineral matter!

Apparently the problem leads to three questions: (1) Is the importance of dust grossly exaggerated? (2) Has the time so commonly assigned to the accumulation of a foot of coal been overestimated? (3) Were the areas which would serve as sources for dust during the coal-forming periods—and especially the Pennsylvanian—exceedingly restricted? The articles cited above emphasize the presence of dust in a way to induce the reader to believe that the importance of atmospheric dust has been overlooked rather than overestimated. If the time allotted for coal formation is fairly accurate, we would be led to believe that the sources and perhaps the means of transportation of dust were very much restricted and that the current evidence for a fairly moist, uniform climate on a land surface heavily covered by vegetation and restricted in area, becomes better established.

WALDO S. GLOCK

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## THE AMERICAN CHEMICAL SOCIETY

(Continued)

DIVISION OF ORGANIC CHEMISTRY

H. T. Clarke, *chairman*

Frank C. Whitmore, *secretary*

*The selective activation of alumina for decarboxylation or dehydration:* HOMER ADKINS. In seeking experimental verification of the idea that the activity of a catalyst for an organic reaction in a heterogeneous system is conditioned by the magnitude of the distance between the atomic nuclei of the solid catalyst, five distinct kinds of alumina have been prepared from the aluminum alkoxides, aluminum hydroxide and hydrated alumina. It has been shown that the size and shape of the alkoxyl group is a determining factor in the relative extent to which decarboxylation or dehydration is induced in esters, alcohols and acids by the alumina prepared from the solid alkoxides. An increase in "molecular porosity,"

<sup>1</sup> Free, E. E.: "Movement of Soil Material by the Wind," U. S. Dept. of Agriculture, *Bull.* 68.

<sup>2</sup> Huntington, E.: "The Pulse of Asia."

<sup>3</sup> Reid, Clement: "Dust and Soils," *Geol. Mag.*, N. S., December, III, Vol. I, 1884, p. 165.

<sup>4</sup> Campbell, M. R.: "The Coal Fields of the United States." General Introduction, *U. S. Geol. Survey, Professional Paper* 100-A.

*i. e.*, of the distances between aluminum atoms in the solid, is favorable to decarboxylation and unfavorable to alkene formation.

*On the synthesis of thiazolidine and thiazane derivatives:* F. B. DAINS, R. Q. BREWSTER, J. S. BLAIR and W. C. THOMPSON. The present report is part of a larger investigation. The immediate object of this part of the work was to devise methods for the synthesis of thiazolidine and thiazane derivatives of known structure. This was accomplished as follows: (1) The addition of mustard oils,  $\text{RNCS}$ , to aryl-allylamines,  $\text{RNHC}_3\text{H}_5$ , formed diaryl-allyl-thioureas, which by the action of acids were converted to 2-aryl-imino-3-aryl-5-methyl thiazolidines. (2) Aryl-N-ethanols,  $\text{RNHCH}_2\text{CH}_2\text{OH}$ , gave with arylisothiocyanates and cyanates ureas which condensed easily to thiazolidines and oxazolidines. (3) From aryl-N-propanols and mustard oils were obtained thioureas and then thiazanes,  $\text{SC}(\text{NR})\text{NRCH}_2\text{CH}_2\text{CH}_2$ . (4) Alpha-arylamino-beta-hydroxyl-gamma-chloro-propane combined with aryl mustard oils to give 5-hydroxythiazanes.

*Urethanes from chlorine-substituted secondary and tertiary alcohols:* LESTER YODER. Certain tertiary alcohols, for example, trichlorotertiary butyl alcohol, which do not react directly with phosgene, give the chlorocarbonates when the dilute solution in benzene is treated with sodium and then with phosgene. The products react readily with ammonia and with aniline chloral condenses with glycerol to form a substituted 1,3-dioxole. The readiness with which this product reacts with phosgene indicates a primary rather than a secondary hydroxyl, hence the assumption of a five-membered rather than a six-membered ring. This dioxole derivative and some of the chlorine substituted urethanes prepared were found to have hypnotic properties.

*Gamma-chloropropyl urethanes and a synthesis of the 1,3-oxazine ring:* ARTHUR W. DOX and LESTER YODER. Gamma-chloropropyl alcohol reacts readily with phosgene to form a chlorocarbonate, and the latter reacts ammonia and with aniline to form the carbamate and the carbanilate respectively. Removal of hydrochloric acid from gamma-chloropropyl carbanilate results in the formation of the six-membered 1,3-oxazine ring. This reaction is analogous to that studied by Otto and by Johnson and Langley in which the beta-halogen alkyl carbanilates lose hydrochloric acid and form the five-membered 1,3-oxazole ring.

*Removal of iodine from aromatic iodo compounds, and its bearing on electromerism:* BEN H. NICOLET and REUBEN B. SANDIN. Several new derivatives of 2-iodo-4-aminotoluene are described.

With stannous chloride and hydrochloric acid, iodine is removed from m-iodoamino derivatives, as well as from o-iodoamino compounds; but the rate of removal is some hundreds of times slower. The results are explained on the basis of a one-sided reaction taking place on a mixture of electromers. The behavior of such a mixture is discussed.

*The spontaneous decomposition of unsaturated aliphatic iodochlorides:* L. B. HOWELL. Previous work (*J. A. C. S.*, 42, 997-9) upon iodochloride-1,2-dichloro-2-iodoethylene and iodochloride-2-chloroethylene has shown that their spontaneous decomposition is not accompanied by loss of chlorine (*cf. Ann.* 369, 135). Further investigation has shown that the expected shift of the 2 Cl atoms from the group  $-\text{ICl}_2$  to the double bond is not the only change involved. Thus, when  $\text{CHCl}=\text{CHICl}_2$  decomposes the products include  $\text{C}_2\text{H}_2\text{I}_2\text{Cl}_2$  and  $\text{C}_2\text{H}_2\text{Cl}_4$  as well as  $\text{C}_2\text{H}_2\text{Cl}_3\text{I}$  (in addition to iodine monochloride and free iodine). Evidently either iodine chloride or chlorine may add to the residue  $-\text{CHCl}-\text{CHCl}-$  or iodine may be entirely replaced and the residue chlorinated. The compound  $\text{Cl}_2\text{ICCl}=\text{CClI}$  upon decomposition gives  $\text{C}_2\text{Cl}_2\text{I}_2$ ,  $\text{C}_2\text{ClH}_3$  and what is apparently a constant boiling mixture of  $\text{C}_2\text{Cl}_6$  and  $\text{C}_2\text{Cl}_3\text{I}$ . Constants for the new halo-ethanes and ethenes have been determined.

*The chlorination of 2-amino-p-cymene:* A. S. WHEELER and J. V. GILES. p-Cymene was obtained from spruce turpentine. It was nitrated at  $0^\circ$  and reduced. The acetyl derivative was chlorinated at room temperature in carbon tetrachloride solution. The product contains one chlorine. This is in position 5 as shown by its conversion into 2,5-dichloro-terephthalic acid. Salts of the chloro aminocymene were prepared. By diazo reaction a new chloro carvacrol was prepared. The amino group was also replaced by the carboxyl group, yielding a new benzoic acid. A new series of dyes was prepared by coupling with the following: phenol, resorcinol, salicylic acid, alpha naphthol, beta naphthol, naphthol-2-sulfonic acid, 1-naphthol-4-sulfonic acid, 2-naphthol-7-sulfonic acid. A variety of colors was obtained, some of great brilliancy. The amino chlorocymene was also coupled with itself, forming a neutral compound. By oxidation a new cuminic acid was obtained.

*The catalytic preparation of divinylacetylene:* J. A. NIEUWLAND. Acetylene is passed into a solution of cuprous chloride (three parts), ammonium chloride (one part) and water (one part). The absorption takes place indefinitely, and when subsequently distilled, a mixture of oils comes

over. The one which distills over at 54° C. is presumably vinylacetylene of the formula,  $\text{CH}_2=\text{CH}-\text{C}=\text{CH}$ . Between 75° and 95° a highly refractive oil, of formula  $\text{C}_6\text{H}_6$ , supposed to be divinylacetylene, comes over. About one kilo of the above liquid is used in each flask. After repeated distillations the mixture continues to absorb the gas even for years without deterioration of the catalyst. About 80 to 110 g. of product are obtained at each distillation. The divinylacetylene forms stable tetra and octobromides which crystallize well from alcohol and have definite melting points. When allowed to stand even in sealed tubes the oil slowly changes to a gel and finally to a solid which is extremely explosive. If the original substance is put back into the copper mixture mentioned above it can be kept indefinitely for use when needed by distilling it off at a temperature not exceeding 13° C. When cupric chloride is added to the mixture dichloroethylene is formed, and no hydrocarbons.

*The application of the Friedel and Craft reaction to non-benzenoid compounds:* JAMES F. NORRIS and RAM PRASAD. Continuation of previous work showed that benzoyl chloride condenses, under the influence of aluminium chloride, with ethylene, propylene, butylene, isobutylene, trimethylethylene and isopropylethylene. The product of the reaction in each case was the unsaturated ketone formed as the result of the replacement of one hydrogen atom in the hydrocarbon by a benzoyl group. Hydrogen chloride addition products of the unsaturated ketones were also formed. Condensation was also effected between benzoyl chloride and malonic ester and diisopropyl. The study of the application of the reaction to saturated hydrocarbons is being continued.

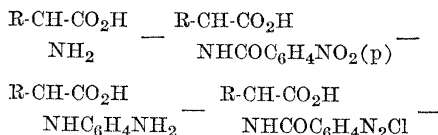
*Some condensations with olefines. A contribution to our knowledge of the Friedel-Craft reaction:* C. E. BOORD and R. S. HANSON. Olefines condense in the presence of anhydrous aluminum or ferric chloride to form oily addition products. These addition products are very reactive, undergoing the following series of transformation: (1) With benzene they form intermediate condensation products which upon hydrolysis yield alkyl benzenes; (2) with phenol they form intermediate condensation products which upon hydrolysis yield alkyl phenols; (3) by direct hydrolysis by cold concentrated hydrochloric acid they yield alkyl chlorides; (4) with acetyl chloride they yield chloro and unsaturated ketones. Ethylene, butylene and amylene give similar results. A scheme of reactions is given

as a simple explanation of the above reactions as well as of the Friedel-Craft synthesis of hydrocarbons. The explanation offered agrees perfectly with that given by Steele for the formation of aromatic ketones by the Friedel-Craft reaction.

*The action of titanium tetrachloride upon certain organic compounds:* JOSEPH F. HASKINS and WILLIAM MCPHERSON. The work described in this paper is the outgrowth of an attempt to prepare an optically active compound of titanium. In the course of this work it was found necessary to study more in detail the fundamental reactions between titanium tetrachloride and representatives of the important groups of organic compounds. The paper gives the results of some of these experiments. Among other reactions, it was found that titanium tetrachloride could be substituted for aluminum chloride with advantage in the synthesis of certain compounds by the Friedel-Craft reaction. For example, benzoyl chloride and benzene in the presence of titanium tetrachloride react to give benzophenone a reaction which serves as a good laboratory method for preparing this substance. The work is being continued.

*A comparison of ferric and aluminum chlorides in their action on chloral, bromal and organic compounds:* G. B. FRANKFORTER and E. E. HARRIS. A continuation of the work of Frankforter and Kritchevsky. The two chlorides have been compared in their condensing properties, using chloral and bromal with the phenolic ethers and other organic compounds. Among the most important compounds prepared are the following: Diphenyltribromoethane, tetrabromodiphenyltetrabromoethane, diphenyldibromoethylene, diphenyldiethoxyethylene, diphenyldiacetoacetylene, dibromophenyldibromoethylene, tetraphenyldimethylacetylene. The properties of these compounds have been carefully worked out in addition to the comparison of the action of the two chlorides in their preparation.

*Optically active dyes:* A. W. INGERSOLL and ROGER ADAMS. A study of the action of optically active dyes on fibers should throw light on the mechanism of dyeing. The preliminary work of which this is a report has involved the study of an easy method for preparing pairs of active dyes. An extremely convenient way has been found by first synthesizing and resolving into optically active isomers certain amino acids, in particular phenyl amino acetic acid. These amino acids can be converted into dyes by the following general reactions which take place very satisfactorily in the laboratory:



Dyes.

*The oxidation of lactose, d-glucose and d-galactose with potassium permanganate:* C. A. BUEHLER and W. L. EVANS. (a) These carbohydrates are oxidized by permanganate solutions to carbon dioxide, acetic acid and oxalic acid, the presence of the latter being determined by the concentration of the alkali present and also by the time of the reaction. The oxalic acid production shows a maximum point and the carbon dioxide a minimum point. (b) Mixtures of d-glucose and d-galactose equivalent to a lactose solution of a given concentration are not oxidized to the same amounts of the reaction products as the disaccharide at the same concentration of alkali. (c) The amounts of the reaction products obtained from the two hexoses at 25° and 50° are not the same, while at 75° they are nearly equal.

*Some relationships of the work on halogenated phenols:* W. H. HUNTER. The work on halogenated phenols at the University of Minnesota gives promise of giving information on the following problems: (1) Substitutes in phenols; (2) oxidation of phenols; (3) reactions of unsaturated radio; (4) rearrangements related to the benzidine rearrangement; (5) relation between para (and ortho) groupings.

*A method of measuring the reactivity of the halogen atoms in organic chlorides:* J. B. CONANT, W. R. KIRNER and A. C. GLENNIE. In order to compare the reactivity of a series of chlorides of the types  $\text{RCH}_2\text{Cl}$ ,  $\text{R}(\text{CH}_2)_2\text{Cl}$  and  $\text{R}(\text{CH}_2)_3\text{Cl}$ , it is necessary to have some reaction whose speed can easily be measured and which will not be attended by side reactions. Alkaline reagents and nitrogen compounds are unsuitable, as they cause the formation of unsaturated and cyclic compounds. Potassium iodide in acetone solution has been found satisfactory. The reaction giving the corresponding organic iodide proceeds smoothly. The amount of inorganic iodide used up can be determined by titration. The results show that the reaction is bimolecular. The temperature coefficient is about normal. The values so far obtained indicate the following relative reactivities at 25° as compared to butyl chloride:  $\text{BuCl}$  1.00,  $\text{MeS}(\text{CH}_2)_2\text{Cl}$  1.64,  $\text{MeS}(\text{CH}_2)_3\text{Cl}$  4.5,  $\text{PhCH}_2\text{Cl}$  149,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$  11,800,  $\text{PhCOCH}_2\text{Cl}$  33,200.

*Molecular structure: Benzene, cyclohexane and naphthalene:* JARED KIRTLAND MORSE. Molecular space is considered discontinuous in such a way that the ratio of the distances between any three points on a straight line is rational. For a given molecule the number of these point positions is restricted by the valency condition that all saturated atoms (carbon and above in atomic number) have eight valency electrons equidistant from the nucleus. By applying these criteria, models have been constructed for cyclohexane, benzene and naphthalene, from which can be derived the geometric properties of the dynamic isomers, the relations between chemically related compounds and the mechanism by which molecules form crystal lattices. For naphthalene the crystal lattice agrees with Bragg's X-ray measurements but not with his molecular theory. Cyclohexane has a simple cubic lattice containing one molecule, benzene a centered orthorhombic lattice containing two molecules. A method for calculating the lattice constants, axial ratios and densities of solid benzene and cyclohexane from the density and crystallographic data for naphthalene is given. Cyclohexane: Calc.—lattice constant  $5.697 \times 10^{-8}$  cm., density (solid) 0.75. Obs. density (liquid) Young 10.7° 0.78715 M.P. 4.7°. Benzene: Calculated; lattice constants  $5.697 \times 10^{-8}$  cm.;  $6.996 \times 10^{-8}$  cm.;  $6.137 \times 10^{-8}$  cm.; density 1.0531; axial ratios 0.814 : 1 : 0.877. Observed; axial ratios Groth 0.799 : 1 : 0.891; density Richards 1.0513. Calculated diameter spherical benzene gas molecule  $6.86 \times 10^{-8}$  cm. Effective diameter on collision from kinetic theory using Schumann's viscosity measurements vapor 20°,  $6.78 \times 10^{-8}$  cm.

*Some derivatives of the lactone produced by condensing cyclo-hexene oxide with malonic ester:* E. C. KENDALL and A. E. OSTERBERG. Tetrahydro benzene adds hypochlorous acid to form ortho-chloro-cyclohexanol. This with sodium hydroxide forms cyclo-hexene oxide, which condenses with sodium malonic ester in the same way that ethylene oxide does. The resulting lactone reacts with additional sodium ethylate giving a product which will react with alkyl halides. The properties of the resulting compounds as well as those of certain nitrogen derivatives obtained from the lactones and ammonia have been studied.

*Derivatives of 2,4-dinitrobenzaldehyde:* T. B. DOWNEY with ALEXANDER LOWY. 2,4-Dinitrobenzaldehyde was condensed with a number of aromatic amines, phenols and their derivatives, giving monomolecular and dimolecular condensation

products. Monomolecular condensations were effected with tolidine (also addition product), p-aminoazobenzene, chloroanilines, etc. Dimolecular condensations were effected with phenol, o-chlorophenol, resorcinol, bromoresorcinol, guaiacol, dimethylaniline, diethylaniline, etc. Some of the products are dyes and indicators.

*The quantitative determination of acetic anhydride:* G. C. SPENCER. The proposed method is based upon the action of acetic anhydride and aniline in cold chloroform. An equivalent amount of acetanilide forms. Slight amounts of alcohol and water as found in U. S. P. chloroform do not interfere. The first attempts were made to separate the acetanilide by washing the chloroform solution with dilute sulfuric acid to remove aniline separating the chloroform solution, and evaporating to dryness in a tared beaker. The gravimetric method was unsatisfactory. The method adopted was to hydrolyze the residual acetanilide with 10 per cent. sulfuric acid and titrate the resulting aniline sulfate with half-normal potassium bromate-bromide solution. Results satisfactory for both high and low concentrations of acetic anhydride.

*The estimation of aliphatic nitrate esters in the presence of certain nitro-aromatic compounds:* WILBERT J. HUFF and RICHARD D. LEITCH.

*On the basis for the physiological activity of certain onium compounds. I. Nitrogen derivatives:* R. R. RENSHAW and J. C. WARE. The possible bases for the different types of physiological action of the simple and the substituted tetraalkyl ammonium compounds are briefly considered. The following new substances are described: Iodo methyl acetate, acetyl formocholine salts, methoxymethyl dimethyl amine, beta-dichloroarsine-ethyl trimethyl ammonium chloride, beta-arsenous oxide-ethyl trimethyl ammonium chloride. Improved methods for the preparation of formocholine and certain other choline derivatives are given.

*Deaminization of methyl-cis-3-amino-1,2,12-trimethyl pentanoate:* GLENN S. SKINNER. The decomposition of this ester with nitrous acid has been carried out on a large scale. Reaction products are formed in the following proportions: Methyl esters of unsaturated acids, 62 per cent.; methyl esters of hydroxy acids, 36 per cent.; methyl esters of chloroacids, 2 per cent. The unsaturated ester upon saponification gave lauronic acid which was identified by conversion to the bromolactone. Three crystalline hydroxy acids have been isolated from the saponification products of the various fractions obtained by distilla-

tion under diminished pressure. One of these acids has a tertiary beta-hydroxyl and is identical with the acid of M. P. 101-2°, obtained by the decomposition of the methyl ester of the trans-isomeric amino acid. A second hydroxy acid of M. P. 121° has a secondary hydroxyl as shown by oxidation with Beckmann's chromic acid mixture. The third hydroxy acid of M. P. 208-10° also has a secondary hydroxyl and is optically inactive. d-Cisamphonolic acid could not be isolated. No ether acid was formed whereas the methyl ether d-cisamphonolic acid constitutes 13 per cent. of the decomposition product of the methyl ester of the trans isomeric amino acid.

*Ammono formaldehydes:* EDWARD C. FRANKLIN. The ammonia analog of formaldehyde, compound of the formula  $\text{CH}_2=\text{N}-\text{CH}_2-\text{N}=\text{CH}_2$ , is only known in the form of its dimer, hexamethylene tetramine. The methods of formation and the properties of hexamethylenetetramine are in harmony with the view that it is a polymeric form of an ammono formaldehyde. Hydrocyanic acid, represented by the form HCN, is also to be looked upon as an ammono formaldehyde. It undergoes polymerizations and condensations, reacts with acid sulfites and hydroxylamine, and otherwise behaves in a manner closely resembling the well-known behavior of ordinary formaldehyde.

*International numberings of ring complexes:* AUSTIN M. PATTERSON and CARLETON E. CURRAN. There is at present no uniform system for numbering parent cyclic compounds. The authors have drawn up a simple set of rules for such numbering, with the avowed purpose of preserving as many as possible of the accepted numberings, while achieving consistency. About three fourths of the numberings used in Richter's "Lexikon," Meyer and Jacobson's "Lehrbuch," and the *Chemical Abstracts* indexes conform to the proposed rules. The matter has been taken up with the proper committees of foreign chemists with encouraging results. If their cooperation can be secured it is proposed to publish a classified collection of known ring complexes, the number of which now approaches a thousand.

*Steric hindrance in the migration of acetyl:* L. CHAS. RAIFORD and CHAS. M. WOOLFOLK. In previous work (*J. A. C. S.*, 41, 2068) one of us has shown that when an ortho acetylaminophenol is benzoylated by the Schotten-Baumann reaction, benzoyl goes to nitrogen, while the acetyl shifts to oxygen. In further study of this behavior the present work was done to learn whether this rearrangement would be prevented by the presence of bromine atoms adjacent to the reacting

groups. Acetyl-benzoyl derivatives were prepared from 2-amino-3,6-dibromo-4-methylphenol, 2-amino-3,5,6-tribromo-4-methylphenol, and 2-amino-3,4,5-tribromo-6-methylphenol. In every case the migration was observed, which seems to indicate that the bromine atoms cause no hindrance. The amino cresols used in this work were secured through the nitration of the corresponding brominated ortho and para cresols. When tetrabromo-o-cresol was nitrated by Zincke's method (*J. Pr. Ch.*, (2) 61, 564) we obtained two isomeric mononitrotribromo-o-cresols, in which we were able to prove that the hydroxyl and nitro radicals occupied ortho and para relationships, respectively, in the two compounds. In this nitration Zincke was able to isolate only one of these substances—the ortho product.

*The hydrolysis of alkyl sulfates.* II: RUSSELL MORGAN and H. F. LEWIS. The hydrolysis of dimethyl sulfate under the influence of acids, alkalis and salts is described and the following conclusions are drawn: (1) The higher the dimethyl sulfate: water ratio in the water hydrolysis, the more rapid the hydrolysis; (2) strong acids in low concentration increase the rate of hydrolysis, but in high concentration retard it; (3) the tendency in alkaline solution is for the second alkyl to come off less easily. No difference between NaOH and KOH in low concentration; (4) acetic acid greatly depresses hydrolysis; (5) salts depress the rate of hydrolysis, even preventing the splitting off of the first group; (6) the only substances acting as positive catalysts are the dilute mineral acids, a large number of which have been studied.

*The interaction of primary aliphatic alcohols and beta-gamma-dibromopropyl-thiocarbimide:* RAYMOND M. HANN. Primary aliphatic alcohols react with this substance to form 2-hydroxy-5-

bromomethyl-thiazoline,  $\text{BrCH}_2\text{—CH—S}$   
 $\text{CH}_2\text{—N=C—OH}$

This result is contrary to that assumed by Dixon and also to the correction of Dixon's work by Gabriel, who assumed that the product was  $\text{BrCH}_2\text{—CH—S}$

$\text{CH}_2\text{—N=C—OEt}$

*Aluminum arylamines:* M. L. CROSSLEY. Aluminum reacts with primary and secondary arylamines producing aluminum arylamines and hydrogen. Tertiary amines do not react with aluminum. Mixtures of the three types of amines can be separated by refluxing with aluminum, distilling off the tertiary amine and recovering the primary and secondary amines from the residue.

The aluminum compounds are readily decomposed by water and alcohol, giving the original amines, aluminum hydroxides and small quantities of secondary products such as diphenylamine. The aluminum compound is very reactive and makes possible the introduction of alkyl and aryl groups under atmospheric pressure.

*The action of nitrogen trichloride upon unsaturated hydrocarbons:* G. H. COLEMAN and H. P. HOWELLS. Nitrogen trichloride reacts with amylene in carbon tetrachloride to form ammonium chloride and nitrogen gas. No more than traces of other nitrogen compounds are obtained. With butylene nitrogen forms, in addition to ammonium chloride and nitrogen, a n-chloroamine in about 20 per cent. yield. When this product is shaken with concentrated hydrochloric acid the chlorine atoms attached to nitrogen are replaced by hydrogen. The resulting amine still contains chlorine attached to carbon. With propylene the reaction takes place more slowly but the products are similar to those from butylene. A possible explanation of the failure of amine formation in case of amylene is offered.

*The equilibrium between benzoin and benzaldehyde:* ERNEST ANDERSON, R. A. JACOBSON and M. J. STUTZMAN. The benzoin condensation is found to be reversible. An equilibrium is reached between benzaldehyde and benzoin when either substance is dissolved in alcoholic sodium cyanide. Both pure substances can be recovered from such solutions. The equilibrium is of the general type  $A = 2B$ . The amounts of benzaldehyde and benzoin present at equilibrium in various mixtures check closely with the amounts calculated from the equilibrium constant.

*Di-beta-hydroxyethyl aniline and some of its derivatives:* F. W. UPSON and D. W. MCLAREN. This substance has been obtained in 70 per cent. yield by refluxing one mol. of aniline with three mols. of ethylene chlorohydrine in the presence of 30 per cent. aqueous sodium hydroxide. The product is obtained by ether extraction and fractional distillation of the extract under reduced pressure. Phenyl morpholine has been obtained by a similar process from beta-beta-dichloro diethyl ether. Di-beta-hydroxyethyl aniline and phomo-morpholine have been coupled with diazotized sulfanilic acid giving color substances related to methyl orange.

*The preparation of pure ortho and para xylenes:* H. T. CLARKE and E. R. TAYLOR. The literature dealing with the separation of the xylenes is contradictory and misleading. It has been found

that fractional distillation, selective sulfonation, crystallization of the sulfonic acids and selective hydrolysis of the xylene sulfonic acids all tend to bring about a partial separation of the three xylenes present in coal tar xylene, but that none of these processes alone is entirely suitable for the isolation of the ortho and para derivatives. A satisfactory procedure is described in which the above processes are combined.

*The preparation of tetramethylene bromide:* C. S. MARVEL and A. L. TANENBAUM. Tetramethylene bromide is a research chemical often needed. Several methods have been devised for its synthesis, but none of these is satisfactory. It has been found possible to obtain the substance easily by the following reactions:  $\text{Br}(\text{CH}_2)_3\text{Br} + \text{C}_6\text{H}_5\text{ONa} \rightarrow \text{Ph-O}(\text{CH}_2)_3\text{Br} + \text{NaCN} + \text{EtOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Ph-O}(\text{CH}_2)_3\text{CO}_2\text{Et} + \text{Na} + \text{EtOH} \rightarrow \text{Ph-O}(\text{CH}_2)_3\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{Ph-O}(\text{CH}_2)_3\text{CH}_2\text{Br} + \text{Br}(\text{CH}_2)_4\text{Br}$ . The yields in the steps are 80, 90, 80, 65, 40 and 40 per cent. respectively. As will be noticed the yields are good in every step except the last, where equal amounts of phenoxybutyl bromide and tetramethylene bromide are obtained. The former can be converted into the latter by prolonged treatment with hydrobromic acid. Hydriodic acid reacts like hydrobromic acid, giving about the same yields of the iodine compounds.

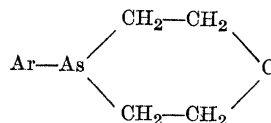
*Some derivatives of ethylbenzene:* F. W. SULLIVAN, JR. Ethylbenzene was prepared in good yield by the action of ethylene on benzene in the presence of aluminum trichloride. It was found that chlorine acts on boiling ethylbenzene giving alpha chloroethyl benzene and not the beta compound as is stated in the literature. The corresponding bromide was prepared. Both give phenyl methyl carbinol on hydrolysis. They also give an acetate when boiled with sodium acetate in glacial acetic acid. Styrene is obtained by passing the vapors of chloroethyl benzene over soda lime. The same substance is obtained in quantitative yield when the chloro compound is heated with quinoline. Ethyl benzene gives very good yields of the nitro derivatives when nitrated according to the standard procedure for the nitration of toluene.

*The preparation of aromatic alpha hydroxy acids and their esters from the cyanhydrins:* G. E. SEIL and IS. KALUGAI. Seil's method of hydrolysis of the cyanhydrins by means of sulfuric acid dihydrate was used on mandelic nitrile prepared from benzaldehyde. The yield of mandelic acid was 83 per cent. The ethyl ester was prepared by different methods. The isopropyl

ester of mandelic acid was synthesized and its properties were determined.

*The preparation of methyl red:* A. W. SCHORGER. Methyl red is prepared by diazotizing anthranilic acid and coupling with dimethylaniline, following in general the procedure of Tizard and Winmill. Free methyl red in the form of violet crystals is best obtained by crystallization from acetic acid, the crystals retaining two molecules of the solvent. From the standpoint of ease of crystallization and purity of product, the best procedure is to crystallize from dilute hydrochloric acid, obtaining the hydrochloride of methyl red. The sodium salt has also been prepared and like the analogous compound, methyl orange, is readily soluble in water.

*New heterocyclic arsenic compounds:* C. S. PALMER. In the presence of two moles of sodium ethylate, one mole of primary arsine condenses with one mole of beta-beta-dichlorodiethyl ether or gamma-gamma-dichlorodipropyl ether to give compounds such as



The products are high-boiling, stable oils. They give the reactions of tertiary arsines, the arsenic readily passing to the pentavalent state by the addition of oxygen, sulfur, halogens, alkyl halides. Chloroplatinates and mercurichlorides are also formed. The above synthesis is a new reaction of primary arsines. Preliminary experiments show that the method can be applied to secondary arsines and to other halides as well as to dihalogenoethers.

*Action of arsenious chloride on quinoline:* JOHN H. SCHMIDT. (By title). Carbostyryl and a product which preliminary analyses indicate to be tricarbostyryl arsonic acid have been prepared by the action of arsenious chloride upon quinoline at comparatively high temperatures. Further investigation of this reaction is in progress.

*On the basis for the physiological activity of certain onium compounds. II. Arsenic derivatives:* R. R. RENSHAW and E. R. WAGNER. Several new arsonium compounds are described. Trimethyl arsine dihalides condensed with ethylene and with formaldehyde to form the arsenic analog of neurine and formaldehyde trimethyl arsonium halides respectively.

*The behavior of the mercuric salts of carboxylic acids toward heat and the structure of mercuric cyanide:* MORRIS S. KHARASCH and

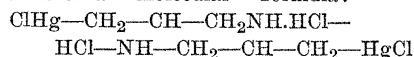


FREDERICK W. STAVELY. The behavior of the mercuric salts of various substituted acetic acids toward heat has been investigated. It has been found that the reaction products depend to a very large extent upon the nature of the substituted groups. In the case of the mercury salts of alkyl substituted acetic acids the mercury either replaces a hydrogen of the alpha carbon atom, or, if there is none available, no reaction takes place (compare, however, the behavior of trichloroacetic acid). In the case of the mercury salts of the phenylated acetic acids the mercury enters the ortho position in the benzene ring. However, upon heating the mercury salts of substituted acetic acids, which lose carbon dioxide upon heating rather easily, a different reaction takes place: the mercury usually taking the place originally occupied by the carboxyl groups. Thus, dimethyl and diethyl acetoacetic acids behave that way. The stability of the various compounds, prepared in the course of this work, towards various reagents has also been studied, and the significance of the tests pointed out.

*The action of mercury on certain alkyl iodides and substituted alkyl iodides:* J. LOUIS MAYNARD. During the present work it has been shown that the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet light but is hastened by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If mercurous iodide is used with methyl iodide, methyl mercuric iodide is formed rapidly. The action of metallic mercury is confined almost entirely to methyl iodide. The use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide. The work is being extended both to a study of the limits of the reaction and of the particular wave lengths which increase the speed of the reaction.

*The structure of the compounds from mercuric salts and olefines:* ROGER ADAMS, F. L. ROMAN, W. M. SPERRY. Two different general formulas have been suggested for the products of mercury salts and olefines, true addition compounds such as  $\text{HOCH}_2\text{CH}_2\text{HgX}$ , and molecular compounds such as  $\text{CH}_2:\text{CH}_2:\text{Hg}(\text{OH})\text{X}$ . The former have been shown to be correct by a study of the action of mercury salts on o-allyl phenols, which give products for which no reasonable "molecular" formulas can be written. o-Allyl phenol reacts with mercuric chloride to form 2-chloromercurimethyl-2,3-dihydro-benzofuran and hydrochloric acid. Treatment of this product with sodium

amalgam gives the corresponding mercuribis compound. Treatment with potassium iodide and iodine gives the corresponding iodomethyl compound which, on reduction, gives 2-methyl-2,3-dihydrobenzofuran. Allyl amine and mercuric chloride give a substance of the following structure which also can not be easily explained on the basis of a "molecular" formula:



*The electromotive force of organic compounds: Aldehydes:* S. B. ARENSON and D. J. BROWN.

*The polymerization of the amylenes:* JAMES F. NORRIS and J. M. JOUBERT. The action of various concentrations of sulfuric acid on the five amylenes was studied. Trimethylethylene and unsymmetrical methylethylene were the most soluble and the most readily polymerized. In the case of these hydrocarbons no alkyl sulfuric acids were formed. The mechanism of the polymerization appears to consist in the dehydration of the alcohol first formed from the hydrocarbon. Isopropylethylene was the only isomer which was polymerized without previous solution in the acid. The study of the products formed as the result of the decomposition of the ozonides of the polymers led to conclusions as to the structure of the dimers of trimethylethylene and isopropylethylene. Improved methods of preparation of the compounds studied were found.

*The relationship between structure and oxidation potential of quinones:* J. B. CONANT and L. F. FIESER. The oxidation-reduction potential of a number of quinones is being measured in alcoholic hydrochloric acid by a titration method. The results at 25°, expressed on the hydrogen electrode scale for certain typical quinones are: benzoquinone 0.711, 1,2-naphthoquinone 0.579, 1,4-naphthoquinone 0.484, phenanthraquinone 0.471, anthraquinone 0.155. Measurements of various derivatives show that substitution of hydrogen by Cl,  $\text{SO}_3\text{H}$ ,  $\text{CO}_2\text{H}$  or  $\text{CO}_2\text{R}$  increases the potential, substitution by alkyl lowers it. The effect of substituents is not entirely cumulative as the following values obtained with chloroquinones show: monochloro 0.736, 2,6-dichloro 0.746, 2,5-dichloro 0.707, tetrachloro 0.695.

*The oxidation of tribromoaniline:* W. H. HUNTER and A. G. MAYERS. The oxidation of 2,4,6-tribromoaniline by chromic acid yields almost quantitatively the 2,4,6-tribromoanil of 2,6-dibromquinone. This reaction may be formulated as a benzidine rearrangement, or as a reaction of unsaturated radicals.

*The oxidation of d-mannose with potassium permanganate:* W. L. EVANS and R. A. CRAWFORD. The oxidation of d-mannose with alkaline potassium permanganate at 50° proceeds with the production of carbon dioxide, oxalic acid and acetic acid. The relative amounts of these products depend on the concentration of alkali used. In neutral solutions only carbon dioxide and acetic acid are formed. At low alkalinities, all three are formed, the carbon dioxide falling off rapidly and the oxalic acid rising rapidly with an increase in alkalinity to about 0.15 N, after which carbon dioxide increases slowly and the oxalic acid decreases slowly to 1.0 N alkali. Above this point the relative amounts of carbon dioxide and oxalic acid remain practically constant. Acetic acid remains almost constant over the whole range.

*Catalytic ammonolysis of beta-naphthol in the vapor state:* A. M. HOWALD with ALEXANDER LOWY. Mixtures of ammonia gas and beta-naphthol vapor were passed over a number of anhydrous oxide catalysts in a Pyrex tube at definite temperatures. A study of the yield of beta-naphthylamine was made as dependent on temperature, catalyst, rate of flow and ratio of reactants. Over a considerable range of conditions, yields in excess of 90 per cent. were obtained, together with some beta-dinaphthylamine. Curves illustrating a marked effect of temperature on catalyst efficiency are shown.

*Deamination of the methyl and ethyl esters of dl-alanine and aminoisobutyric acid:* A. L. BARKER and GLENN S. SKINNER. The methyl and ethyl esters of aminoisobutyric acid yielded largely the esters of alpha-methyl acrylic acid together with a small amount of hydroxy isobutyric acid. The methyl ester yielded 3 per cent. of acid material which contained, according to the Zeisel determination, 70 per cent. of the ether acid. The ethyl ester yielded 0.5 per cent. of acid material which contained 30 per cent. of ether acid. The esters of alanine yielded the unsaturated, chloro and hydroxy esters together with a high boiling nitrogenous residue. The methyl ester gave 15 per cent. of acid material, of which 60 per cent. was the ether acid. The ethyl ester gave 2 per cent. of acid material containing 70 per cent. of ether acid.

*The recovery and refining of pyridine:* WILBERT J. HUFF.

*Intermediate complex formation and electronic valence:* BEN H. NICOLET. Ortho and para iodoamines have their iodine in a mobile state which may be described by calling the iodine "posi-

tive." Two nitro groups, when o-p, produce an even more recognizably negative halogen. But, although two nitro groups thus exceed one amino group, 3,5-dinitroiodobenzene shows no test for positive iodine; and yet, 3,5-diamino-chlorobenzene, boiled with alcoholic sodium ethylate, shows no trace of negative chlorine. It is concluded that certain conditions favoring formation of necessary "intermediate complexes" are necessary for reaction, and that such considerations must be taken into account in judging electronic structures.

*The catalytic synthesis of the acetals and their halogenation:* JOSEPH S. REICHERT, JAMES H. BAILEY and J. A. NIEUWLAND. The acetals were prepared by passing acetylene into the corresponding alcohols in the presence of concentrated sulfuric acid and a mercury salt as a catalyst. The products of the chlorination and bromination of dimethyl and diethyl acetals were determined. The chlorination of diethyl acetal gave a good yield of chloral. Chloral was also prepared by the successive action of acetylene and chlorine on ethyl alcohol. After the required amount of acetylene had been absorbed, the reaction mixture was chlorinated directly without the separation of the acetal. In this process one mol. of acetylene takes the place of one mol. each of alcohol and chlorine as compared to the ordinary process of making chloral from alcohol.

*New derivatives of 2-bromo-5-hydroxy-1,4-naphthoquinone:* ALVIN S. WHEELER and B. NAIMAN. The preparation of 2-bromo-juglone as given by Wheeler and Scott was improved upon. Its benzoate was prepared. Its bromine was replaced by chlorine by means of alcoholic hydrochloric acid. The benzoate of the chloro compound was prepared. A dibromojuglone was made by brominating a hot glacial acetic acid solution of the monobromo compound. The second bromine entered the quinone ring and none entered the phenol ring in spite of the fact that juglone readily takes up two in the quinone and one in the phenol ring. Both bromines can be replaced by chlorine by means of alcoholic hydrochloric acid. Acetates and benzoates were prepared.

*The polymers of pinene. II:* G. B. FRANKFORTER and BETTY SULLIVAN. Improved methods have been worked out for the preparation of the compounds already described, namely, colophene, (C<sub>16</sub>H<sub>16</sub>)<sub>2</sub>, and colophonene, (C<sub>16</sub>H<sub>16</sub>)<sub>5</sub>, together with new derivatives of the same. In addition to the above, new compounds have been obtained which complete the series, namely, the

sesquicolophene,  $(C_{10}H_{16})_3$ , and the dicolophene,  $(C_{10}H_{16})_4$ . The properties of the latter resemble the former in their remarkable stability and in the difficulty with which they form derivatives.

*Some sulfonic acid esters of phenylazophenol and its substitution derivatives:* C. E. BOORD, M. D. COULTER and HELEN L. WIKOFF. (Lantern). Several esters of benzene sulfonic acid, p-toluene sulfonic acid and alpha naphthalene sulfonic acid with phenylazophenol and its substitution products were prepared by the Baumann-Schotten method. The twenty-one esters thus prepared for the first time, together with the fourteen previously described (*Ber.*, 28, 800, 31, 1782, 2116; *J. Pr. Ch.*, 78, 386), are all stable, easily purified, beautifully crystalline compounds melting between 50° and 200°. It is suggested that this type of derivative may be of value in characterizing the sulfonic acids. The para derivatives such as p-tolylazophenol and p-chlorophenylazophenol seem best adapted to this purpose.

*Practical preparation of oxalic acid from acetylene:* SISTER MARY LUCRETIA, LEO J. HEISER and J. A. NIEUWLAND. Oxalic acid can be prepared on a practical scale by passing acetylene into a mixture containing three volumes of nitric acid to one volume of water and about two per cent. mercuric nitrate. The formation and loss of nitrogen oxides in the reaction prevents the commercial use of the process. The reaction proceeds through the formation of an intermediate compound which yields aldehyde, which is then oxidized to oxalic acid. Oxalic acid can be prepared by the direct action of nitrogen oxides on acetylene, by the action of acetaldehyde with nitric acid (3 : 1), and by the action of nitrogen oxides on aldehyde vapor. Acetaldehyde can be prepared by the action of acetylene on dry mercuric nitrate, by the action of acetylene on the compound obtained by treating metallic mercury with nitrogen oxides.

*The oxidation of propylene glycol with lithium, sodium and potassium permanganates:* E. C. HYTREE and W. L. EVANS. (a) Propylene glycol is oxidized by neutral permanganate solutions to carbon dioxide and acetic acid at 25° and 50°. Above certain minimum concentrations of alkali oxalic acid is also obtained. (b) The amount of each oxidation product at low alkalinities is influenced not only by the concentration of the alkali, but also by the use of either lithium, sodium and potassium hydroxides in connection with each of the several permanganates.

*Herabromodiphenyldisulfide:* W. H. HUNTER

and A. H. KOHLHASE. This compound is obtained by treating the silver salt of tribromothio-phenol with iodine in benzene solution. This action is normal, and by so much is contrary to the action of iodine on the salts of halogenated phenols to form polyphenylene oxides. Further, molecular weight determinations in various solvents give consistently low results, apparently showing dissociation of the substance and consequent existence of the free radical  $C_6H_2Br_3S$ , which does not lose halogen spontaneously.

*Formation of goumaric acids and substituted gamma-butyric acids from resorcinol, orcinol and phloroglucinol:* W. D. LANGLEY and ROGER ADAMS. While attempting to prepare certain complex ketones, it was found that beta-chloropropionitrile and gamma-chlorobutyronitrile do not condense with resorcinol, orcinol or phloroglucinol in the presence of zinc chloride and hydrogen chloride as nitriles ordinarily do to give ketones, but instead condense to give acids,  $(HO)_2C_6H_3CH_2CH_2CO_2H$ , etc. Alpha-beta-unsaturated nitriles give the same type of condensation product, indicating without doubt that with these compounds the first step is the addition of hydrogen chloride to the double bond.

*A new method of preparing unsaturated 1,4-diketones:* J. B. CONANT and R. E. LUTZ. Substances of the general type  $RCOCH=CHCOR$  are of interest because they contain the characteristic linkage of quinone and indigo. Only a relatively few representatives have been previously prepared and the methods of preparation are difficult. We have prepared a number of aryl unsaturated 1,4-diketones by the action of fumaryl chloride, aluminum chloride, and an aromatic hydrocarbon. The yields are good. It is interesting that these substances are all smoothly reduced to the corresponding ethane derivatives by sodium hydrosulfite or titanous chloride in contrast to ketones of the type  $RCH=CHCOR$ , or acids of the type  $HO_2CCH=CHCO_2H$ , which are not reduced by these reagents.

*The preparation of hydroxypyruvic acid:* W. L. EVANS and G. P. HOFF. The following steps were used: (1) pyruvic acid, (2) monobromopyruvic acid, (3) its methyl ester, (4) methyl ester of hydroxypyruvic acid, (5) hydroxypyruvic acid. The conversion of (3) to (4) was accomplished by means of methyl alcohol and potassium formate, (5) is easily obtained from a slightly acidulated aqueous solution of (4).

CHARLES L. PARSONS,

Secretary